CRPAQS Fog and Chemistry Analysis Results

Information for Development of PM2.5 Conceptual Model

S. D. Ziman

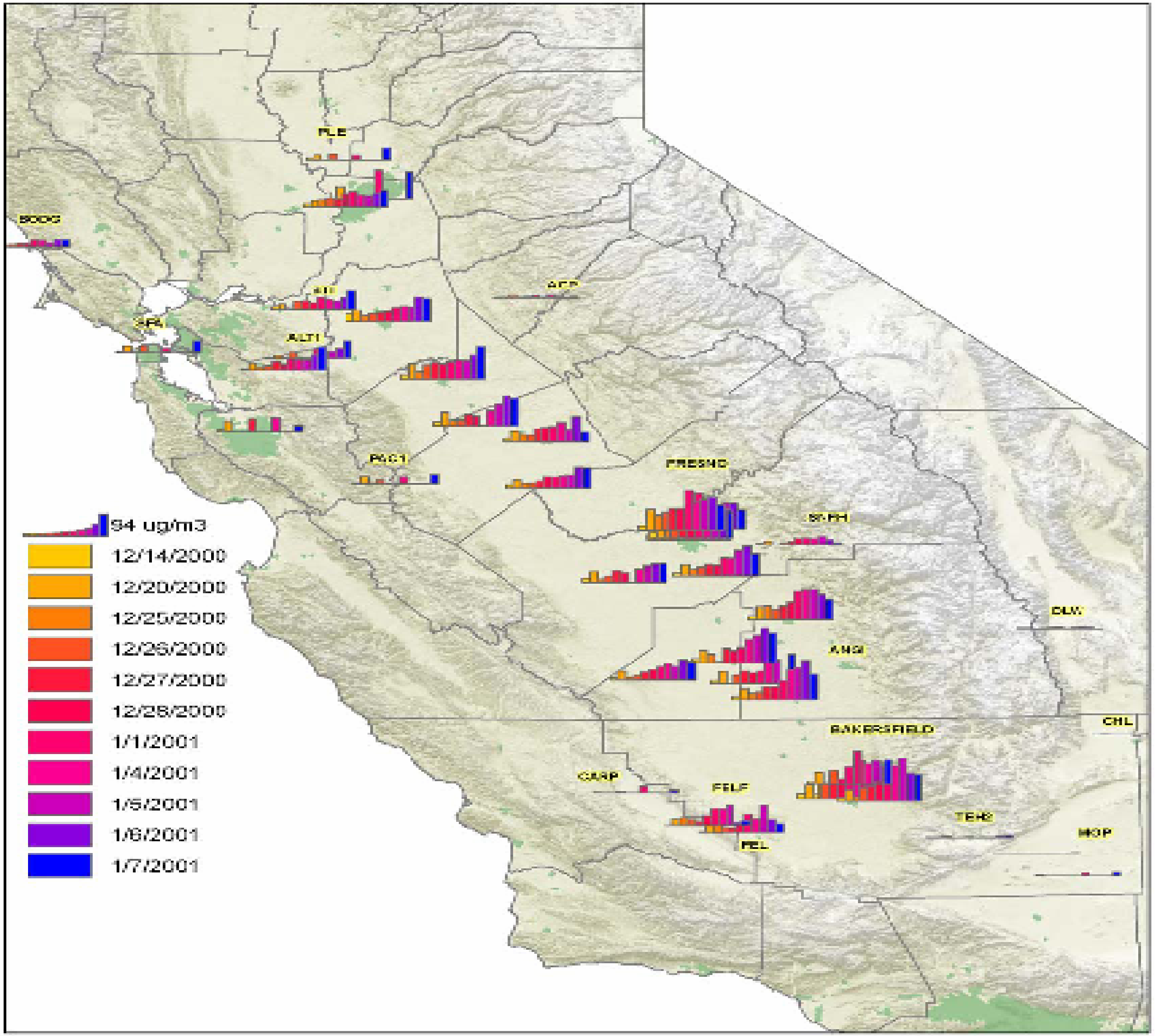


Figure 2. $PM_{2.5}$ concentrations ($\mu g/m^3$) from December 14, 2000, through January 7, 2001, at CRPAQS monitoring sites. Note that measurements are not available or not shown for multiple days between December 14, 2000, and January 7, 2001.

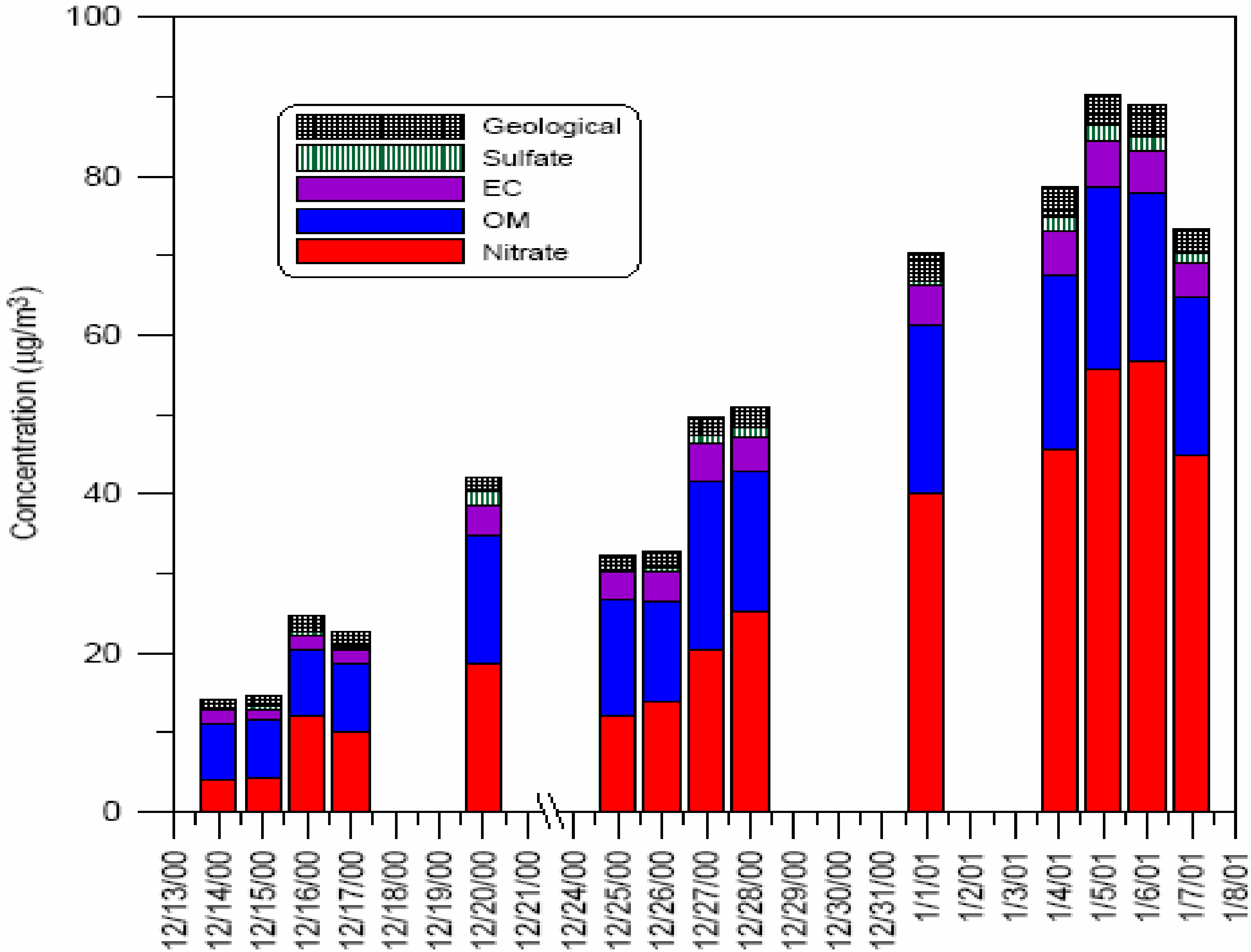


Figure 3. Daily concentration ($\mu g/m^3$) of $PM_{2.5}$ chemical components averaged across the SJV sites for 15 representative days between December 14, 2000, and January 7, 2001.

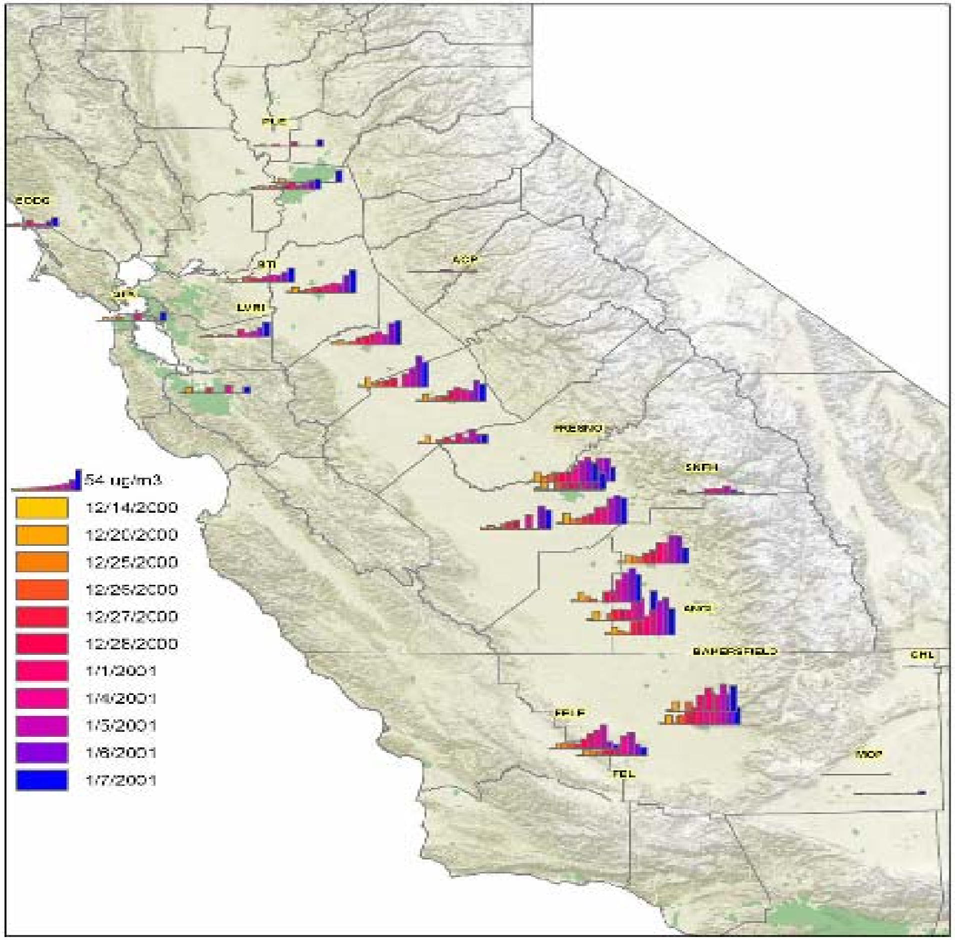


Figure 4. Particulate ammonium nitrate concentrations ($\mu g/m^3$) from December 14, 2000, through January 7, 2001, at CRPAQS monitoring sites. Note that measurements are not available or not shown for multiple days between December 14, 2000 and January 7, 2001.

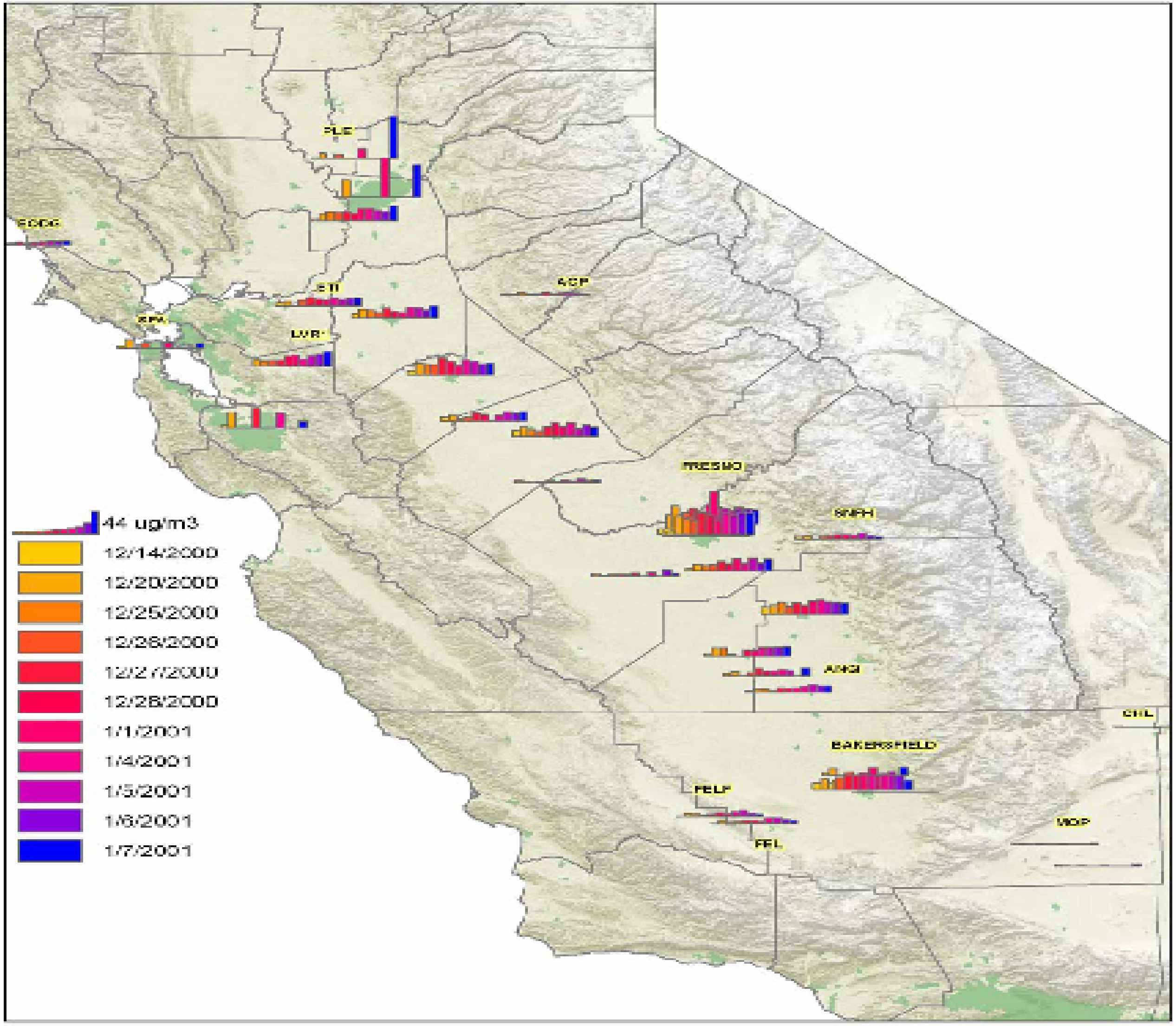


Figure 5. Particulate OM concentrations ($\mu g/m^3$) from December 14, 2000, through January 7, 2001, at CRPAQS monitoring sites. Note that measurements are not available or not shown for multiple days between December 14, 2000, and January 7, 2001.

Nitric Acid Formation Pathways

- Daytime: $NO_2 + OH \rightarrow HNO_3$
- Nighttime: $NO_2 + O_3 \rightarrow NO_3 + O_2$
- $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$
- $N_2O_5 + H_2O$ (g or aq) $\rightarrow 2HNO_3$

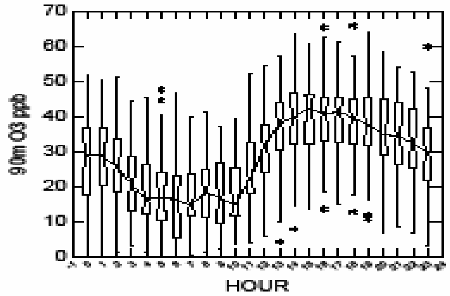


Figure 3. Box whisker plot of hourly (PST, begin hour) ozon

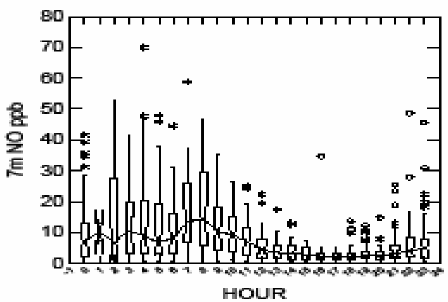


Figure 4. Box whisker plot of hourly (PST, begin hour) NO (

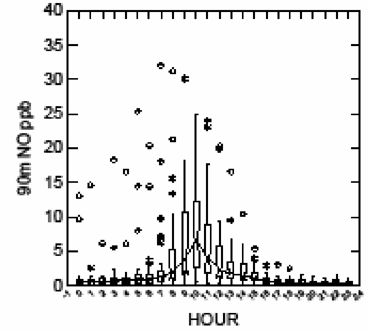


Figure 5. Box whisker plot of hourly (PST, begin hour) NO (ppb) at 90 m.

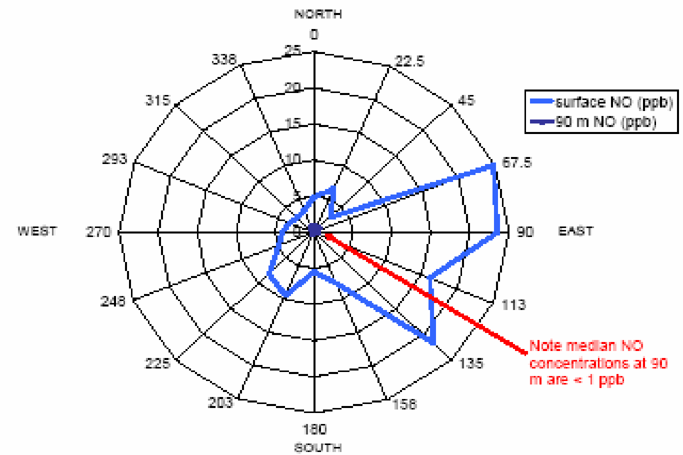
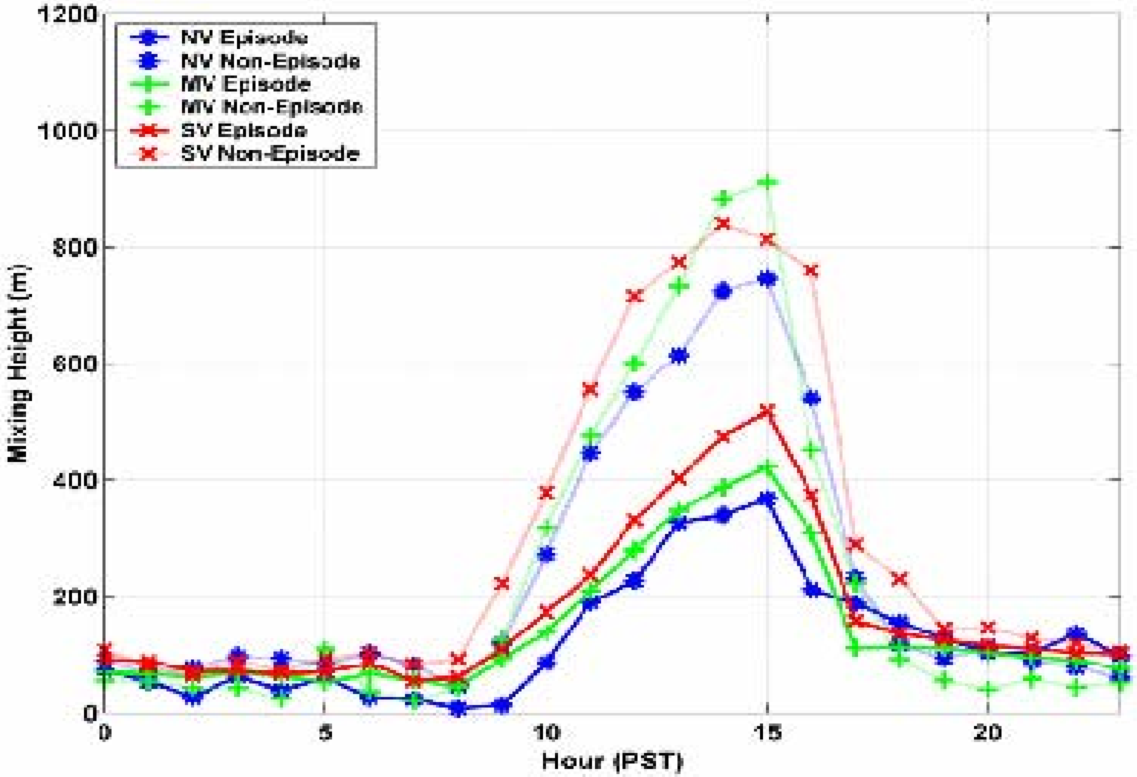


Figure 6. Median NO concentration (ppb) at 90 m and at 7 m at night (2200-0500 PST) by 100-m and 7-m wind direction, respectively.

Figure 4. Mean diurnal mixing heights on episode and non-episode days for the NV, MV, and SV from November 15, 2000, through January 31, 2001.



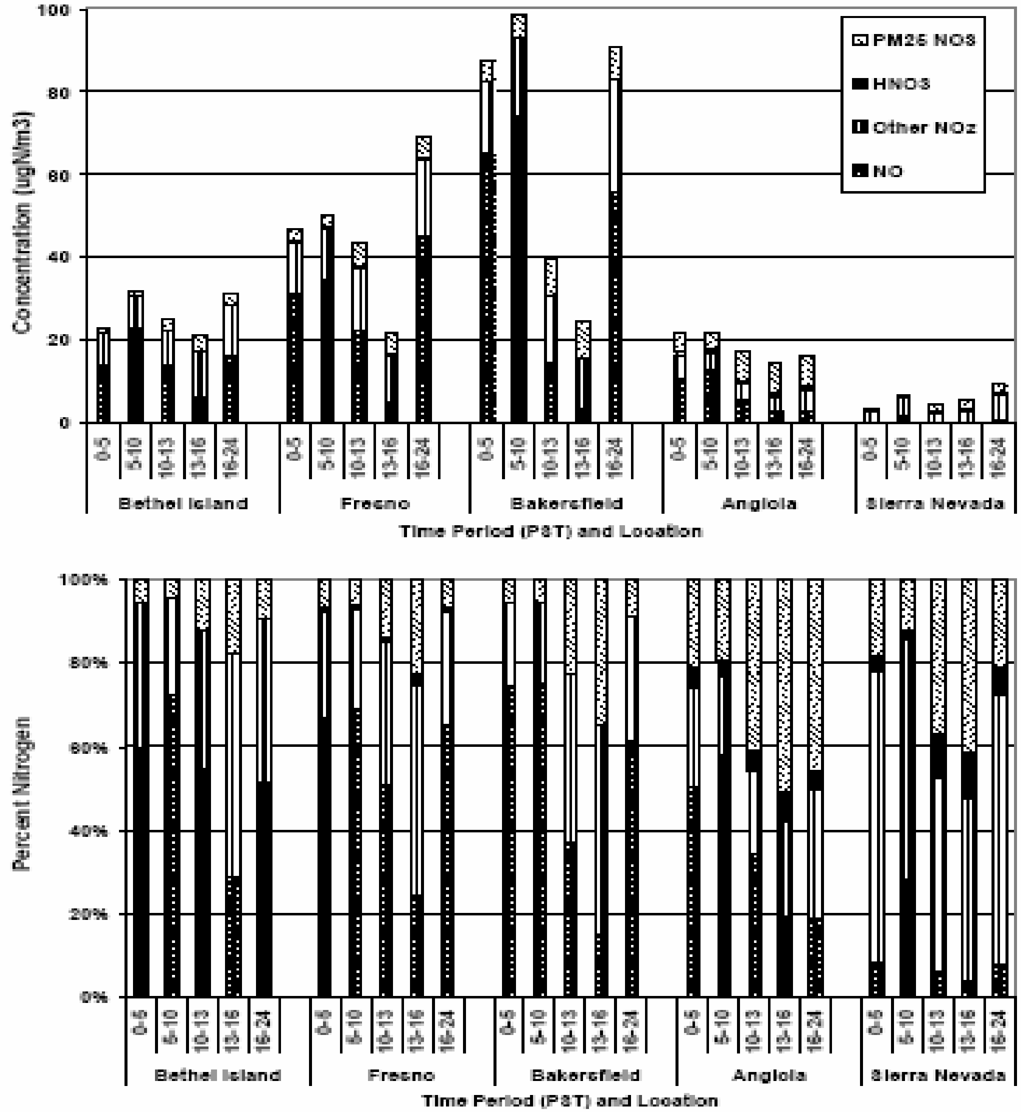


Figure 3. The 15-day average concentrations (top) and relative distributions (bottom) of NO_x-related compounds by sampling period at the five CRPAQS core air monitoring sites in winter.

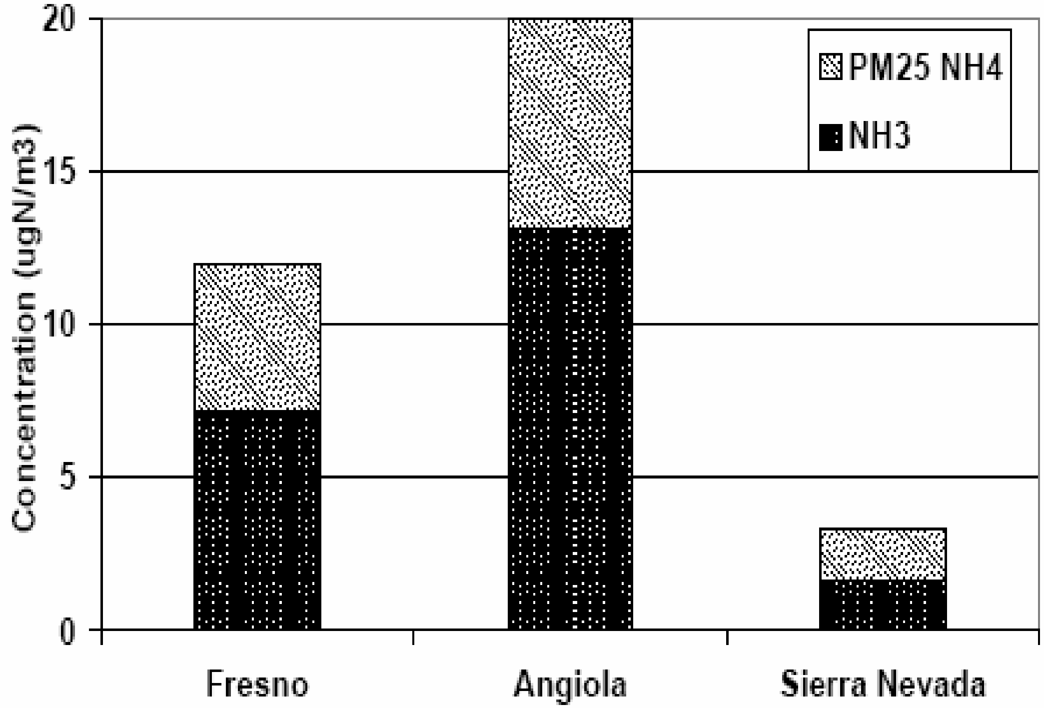


Figure 4. The 15-day average distribution of ammonia-related compounds at Fresno, Angiola, and Sierra Nevada Foothills in winter.

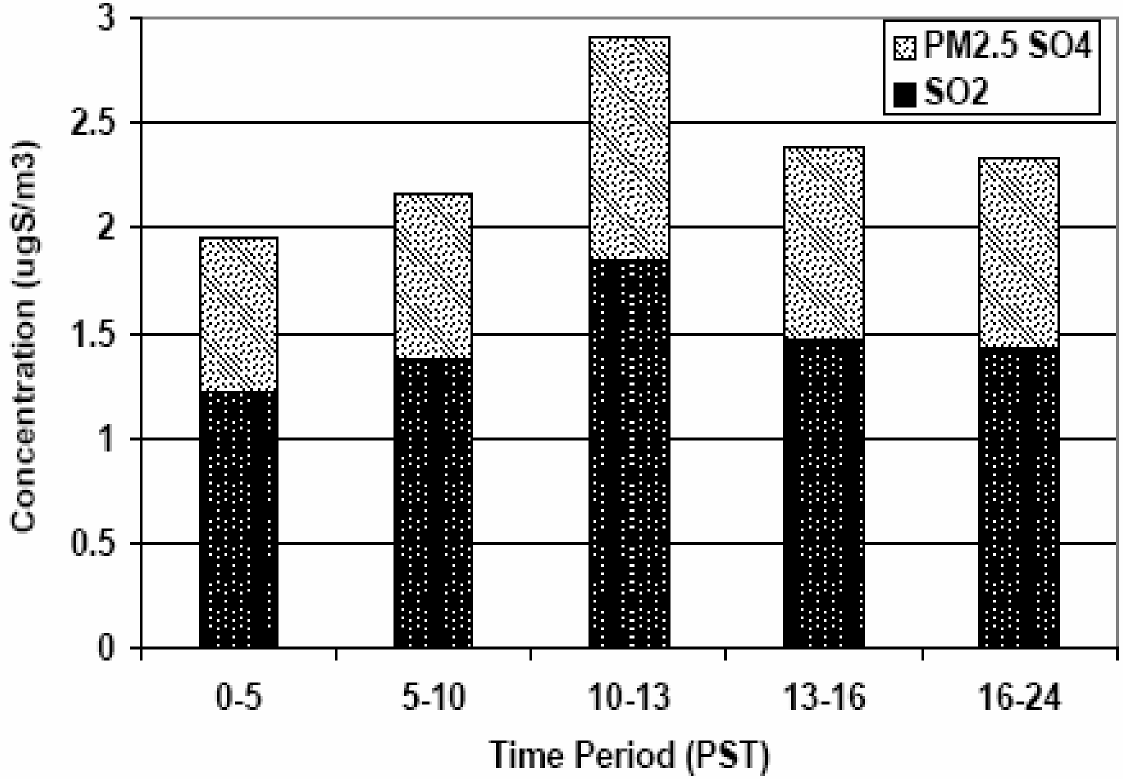


Figure 5. The 15-day average distribution of SO_2-related compounds in Bakersfield in winter.

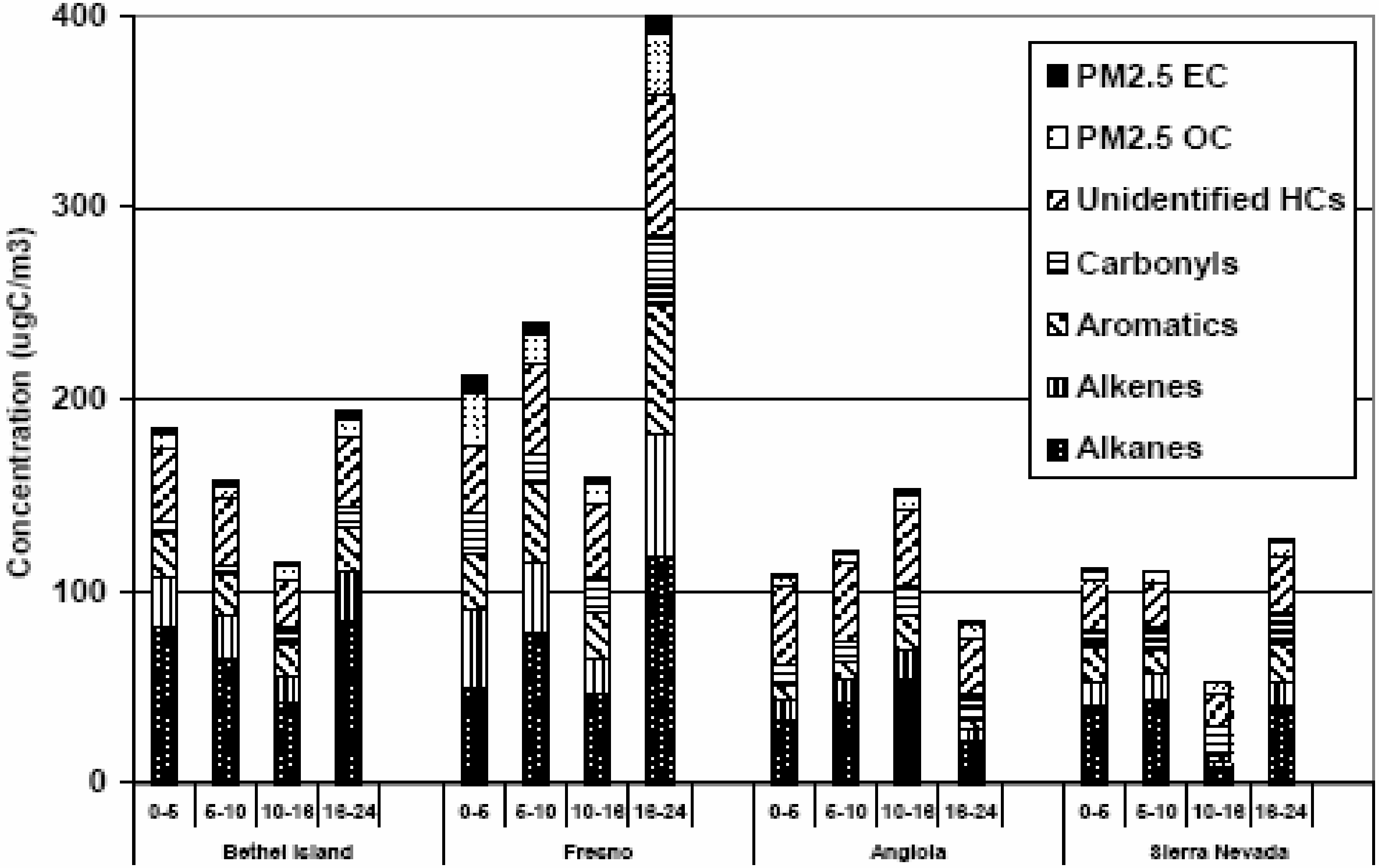


Figure 7. The 15-day average distribution of carbonaceous compounds by sampling period at four CRPAQS core air monitoring sites in winter.

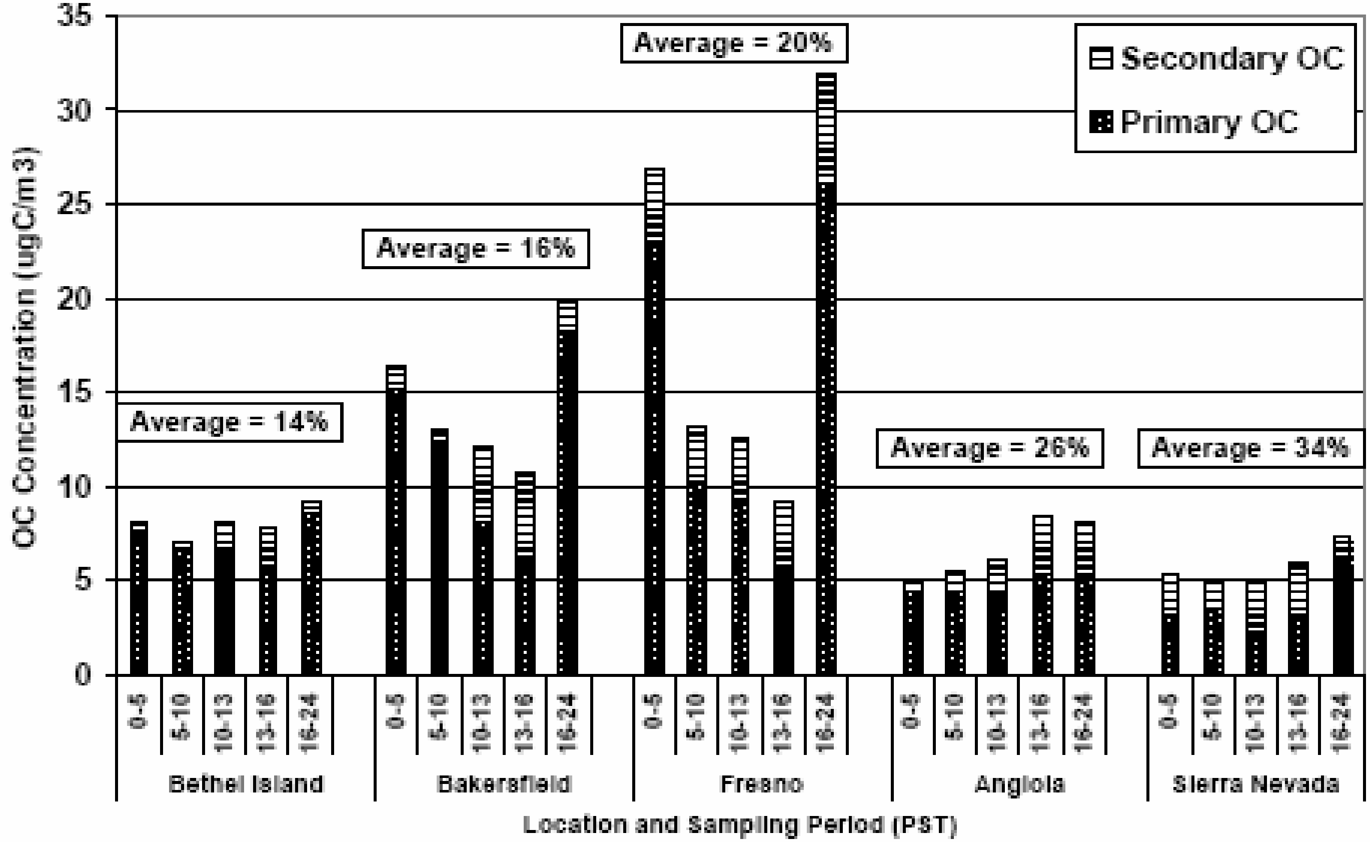
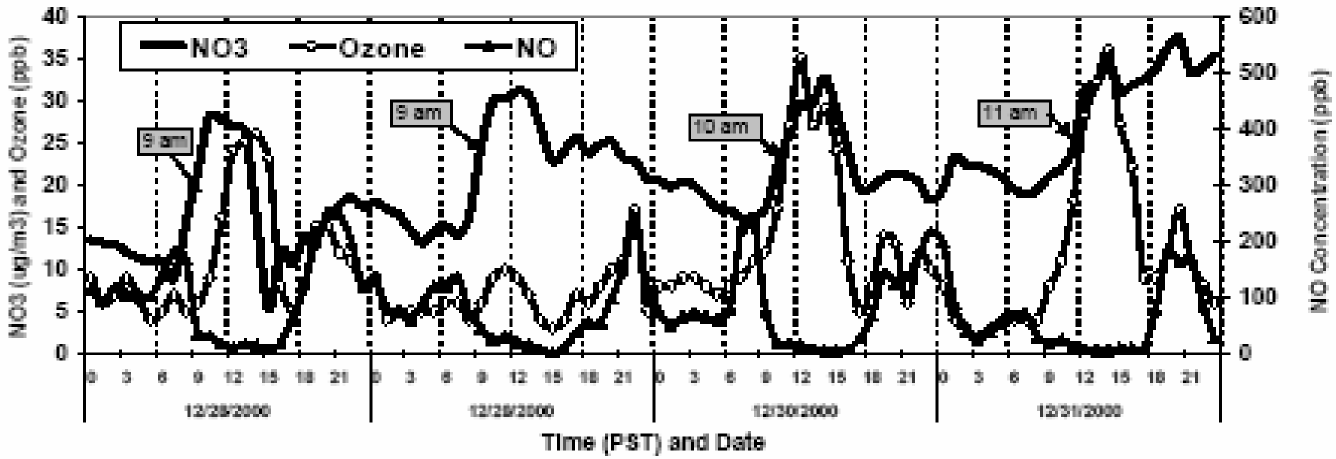


Figure 10. Average estimated distribution of primary and secondary OC by sampling period at the five CRPAQS core sites on 15 days in winter.



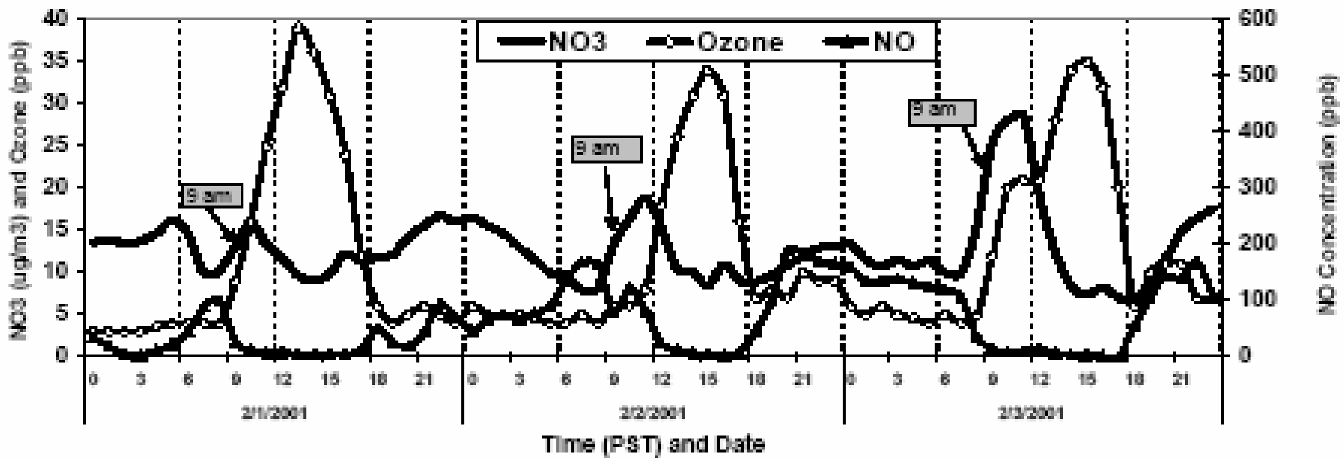


Figure 14. Hourly concentrations of NO, O_3, and $PM_{2.5}$ NO_3 in Fresno on December 28-31, 2000 (top), and February 1-3, 2001 (bottom).

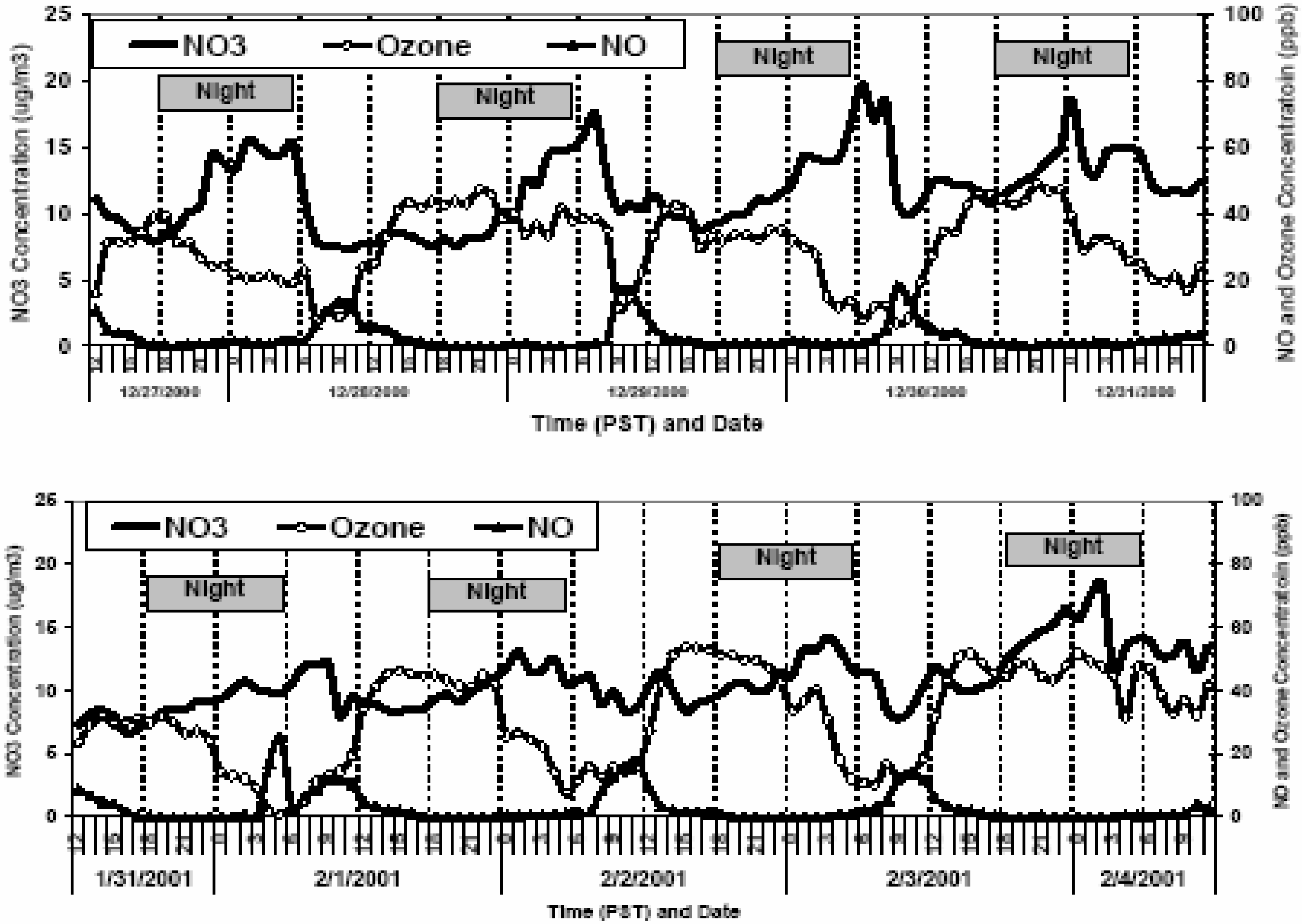


Figure 15. Hourly concentrations of NO, O_3, and $PM_{2.5}$ nitrate at 90 m elevation on a tower in Angiola on December 28-31, 2000 (top), and February 1-3, 2001 (bottom).

Conclusion on Nitrate Production

Continuous aerosol nitrate data, in conjunction with NO and ozone data, suggest both the daytime and nighttime nitric acid formation pathways are active in the SJV. Observations at 90m above the surface in rural Angiola indicate up to 10 µg/m3 aerosol nitrate can be produced aloft in 6 to 12 hours at night. Increases in aerosol nitrate aloft, especially from sunset to midnight, are fairly common in December and January. Surface measurements in Fresno show rapid increases in aerosol nitrate during the late morning that coincides with rapid decreases in NO and increases in O3, suggesting aerosol nitrate is being entrained from aloft as the mixing height rise in the morning. Valleywide nighttime production of ammonium nitrate aloft followed by daytime entrainment into the surface layer are the likely processes that explain the unusually high spatial homogeneity of wintertime ammonium nitrate levels in the Valley.

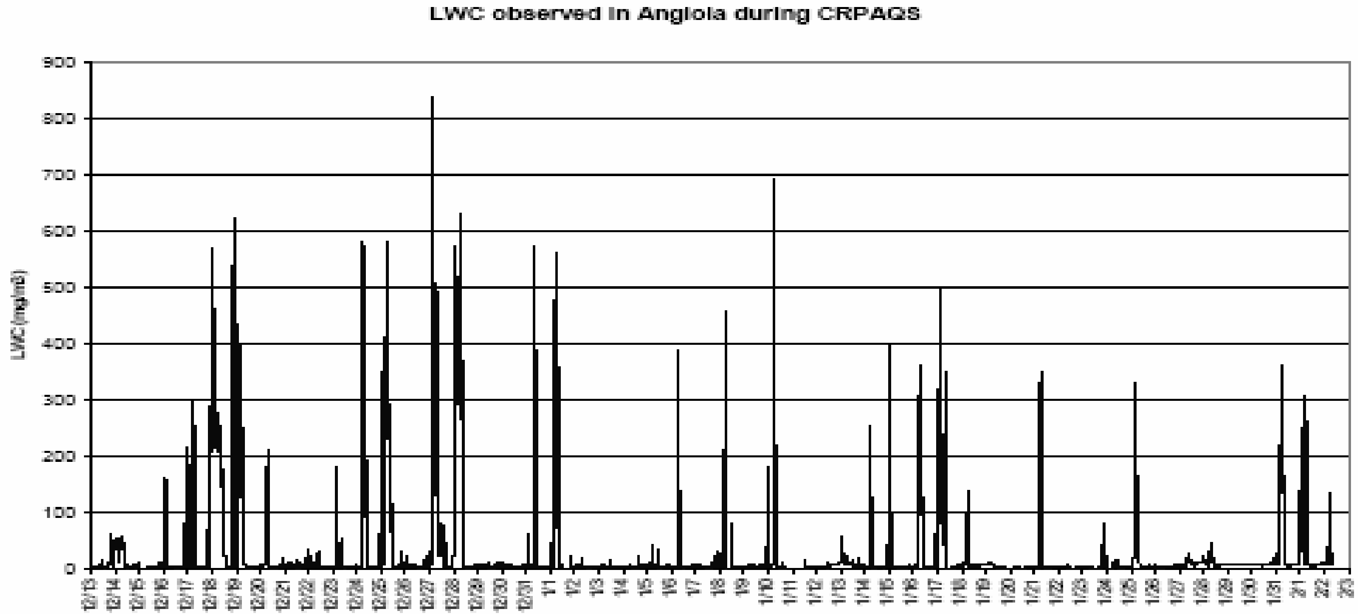
Yet to be resolved questions on nitrate formation

- Nitrate is limiting relative to ammonia
- NO needs to be reduced for both daylight and night time formation
- Much NO, NO_2 available in gaseous phase than nitric acid.
- So, what is controlling precursor for ozone, OH production?

Fog Chemistry

- Provides heterogeneous mechanisms for SO_2 oxidization
- Drops have large amounts of ammonia, resulting in higher pH (5-8)
- More recent measurements show decrease in SO_2
- Aqueous phase reaction with dissolved VOCs may be important in formation of secondary organic, but not proven, and:
  - OC more efficiently scavenged than EC, and there are differences within OC scavenging, with wood smoke scavenged faster than auto related OC
  - But if chemistry occurs, may be more SOA after fog dissipates

Figure 1



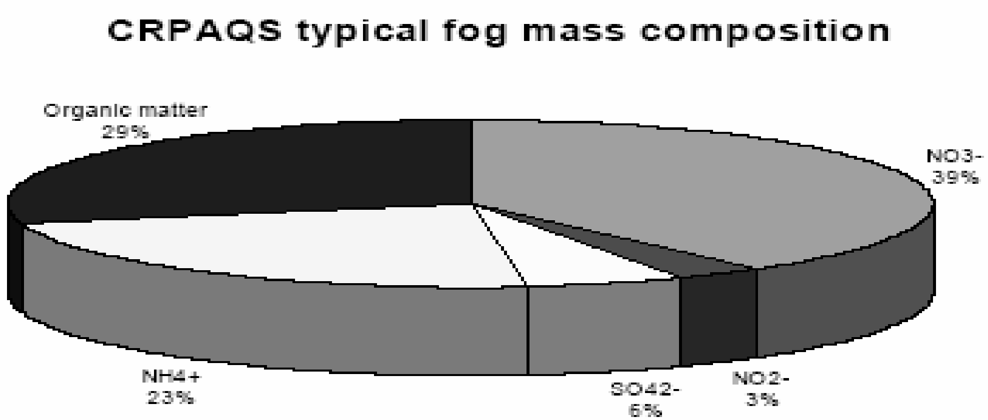
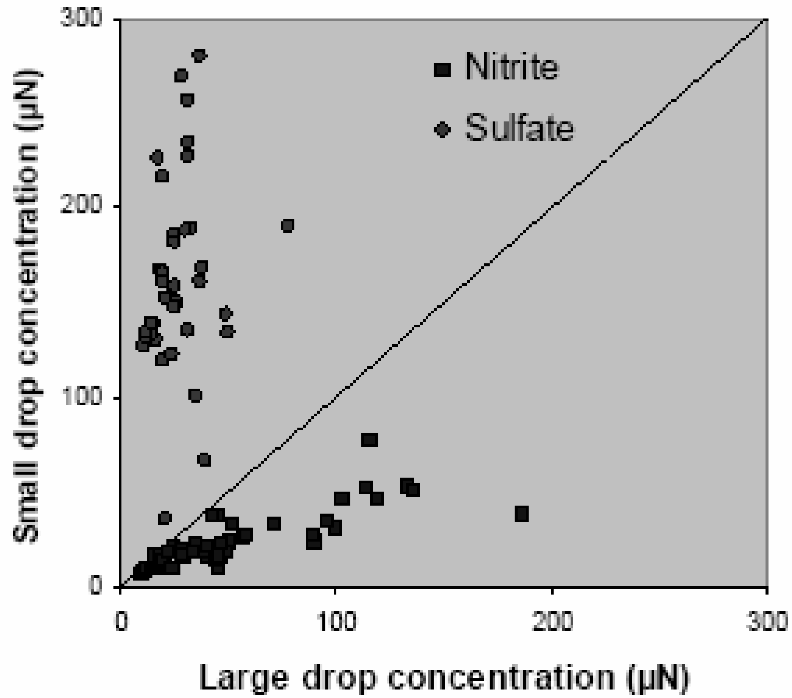
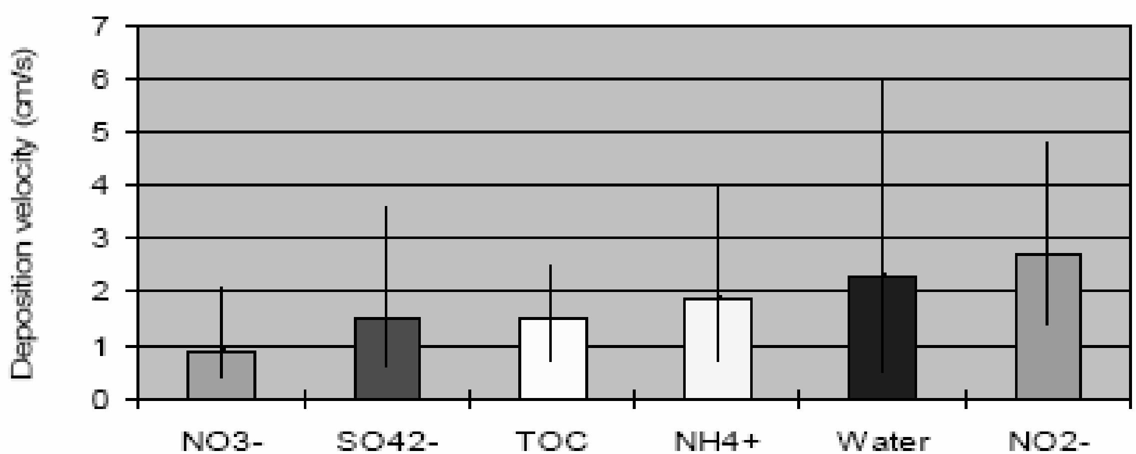


Figure 2

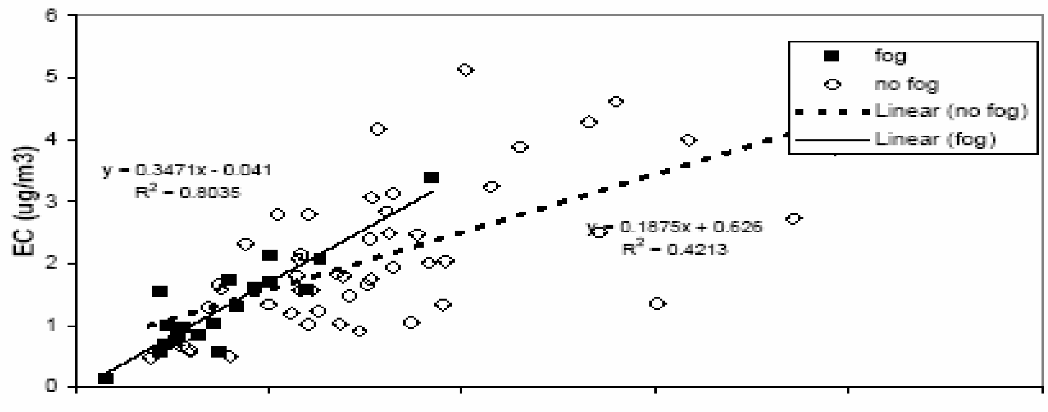
Figure 3



Nitrite
Sulfate
Small drop concentration (µN)
Large drop concentration (µN)
0
100
200
300
0
100
200
300



Deposition velocity (cm/s)
0
1
2
3
4
5
6
7
NO3-
SO42-
TOC
NH4+
Water
NO2-



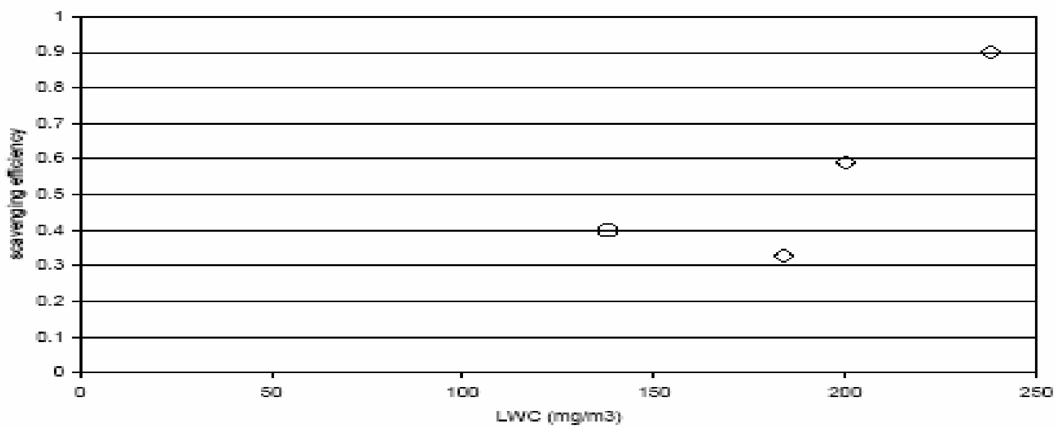


Figure 3. Total Carbon (TC) Scavenging efficiencies as a function of Liquid Water Content (LWC), circles represent data from Fresno, diamonds represent data from Angiola.